

# Anderson Model in a Superconductor: $\Phi$ -Derivable Theory

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## Abstract

We introduce a new  $\Phi$ -derivable approach for the Anderson impurity model in a BCS superconductor. The regime of validity of this conserving theory extends well beyond that of the Hartree-Fock approximation. This is the first generalization of the  $U$ -perturbation theory to encompass a superconductor.

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The Anderson impurity model [1] provides one of the most versatile field-theoretic descriptions for interacting correlated electrons within condensed-matter physics [2]. The Anderson hamiltonian in a normal metal is

$$\mathcal{H}_A = \mathcal{H}_s + \mathcal{H}_{sd} + \mathcal{H}_d + \mathcal{H}_U, \quad (1)$$

where  $\mathcal{H}_s = \sum_{k,\sigma} \varepsilon_{k\sigma} n_{k\sigma}$  describes the electron gas,  $\mathcal{H}_{sd} = \sum_{k,\sigma} (V_k c_{k\sigma}^\dagger d_\sigma + V_k^* d_\sigma^\dagger c_{k\sigma})$  is the admixture interaction,  $\mathcal{H}_d = \sum_\sigma E_\sigma n_\sigma$  represents the  $d$ -electron level and  $\mathcal{H}_U = U n_\uparrow n_\downarrow$  denotes the Coulomb-repulsion interaction. This model describes the continuous transition of a nonmagnetic resonant level (for  $U \ll \Gamma$ , where  $\Gamma = \pi N(0) \langle |V|^2 \rangle$ ) to a magnetic atom ( $U \gg \Gamma$ ), and one can consider treating either  $V$  or  $U$  perturbatively. For  $\Gamma/U \ll 1$ , in the magnetic Schrieffer-Wolff (SW) limit [3], the Anderson hamiltonian reduces to the  $s-d$  hamiltonian, *i.e.*, the Kondo model. This limit and the magnetic-nonmagnetic transition have been successfully treated within the renormalization group (RNG) program [4]. However, simpler controlled approaches would be highly desirable due to the wide applicability of the Anderson model and its variants to many physical systems of interest.

After its initial introduction to describe the nonmagnetic-magnetic transition of impurities in otherwise nonmagnetic metals, and the associated many-body Kondo phenomenology, the Anderson model has been extensively applied and generalized to also describe interacting pairs of impurity atoms in metals (the Alexander-Anderson model), valence fluctuations and heavy-fermion materials (the periodic Anderson model), chemisorption (the Anderson-Newns model) and charging phenomena and Coulomb blockade in quantum dots and quantum-dot arrays. It is also of great inherent interest to consider the Anderson model in a superconductor and the appropriate theoretical approaches to this problem. In particular, the RNG approach has not been generalized to this case and the Bethe-Ansatz (BA) method fails to be suitable since the superconducting electronic spectrum does not fulfill the requirement of a linear ( $\varepsilon_k \propto k$ ) dispersion relationship, necessary for the applicability of the  $k$ -state enumeration within the BA scheme.

Yosida and Yamada [5] first pointed out that in order to obtain the single-particle Green's function and the local density of impurity  $d$ -states, it is useful to study the many-body perturbation theory with respect to  $U$ . Thus one considers the Anderson hamiltonian as

$$\mathcal{H}_A = \mathcal{H}_{HF}^0 - U \langle n_\uparrow \rangle \langle n_\downarrow \rangle + \mathcal{H}'_U, \quad (2)$$

where  $\mathcal{H}_{HF}^0 - U\langle n_\uparrow \rangle \langle n_\downarrow \rangle$  is up to the constant energy shift,  $U\langle n_\uparrow \rangle \langle n_\downarrow \rangle$ , the unperturbed Hartree-Fock (HF) hamiltonian and

$$\mathcal{H}'_U = U\delta n_\uparrow \delta n_\downarrow = U(n_\uparrow - \langle n_\uparrow \rangle)(n_\downarrow - \langle n_\downarrow \rangle) \quad (3)$$

is the Coulomb-repulsion term, treated as the perturbation, see Fig. 1. Yosida and Yamada, in their original paper [5], used a complicated formalism utilizing Pfaffian determinants to derive the  $U$ -perturbation theory; Yamada [6] first presented the numerically evaluated  $d$ -electron spectral density function using the  $U^2$  selfenergy in the low-temperature limit. This approach may easily be generalized to arbitrary temperatures in normal metals [7], for which one may introduce the  $d$ -electron impurity selfenergy  $\Sigma_N(\omega)$  through

$$G_N(\omega) = \left( (G_{HF})^{-1} - \Sigma_N(\omega) \right)^{-1}. \quad (4)$$

Here the HF propagator is

$$G_{HF}(\omega) = -\left( \omega - E_{HF} - F(\omega) \right)^{-1}, \quad (5)$$

with  $F(\omega) = \sum_k |V_k|^2 G_k^0(\omega) \approx -i\Gamma$  and  $G_k^0(\omega) = (\omega - \varepsilon_k)^{-1}$ . Above,  $E_{HF} = U + \langle n \rangle$  is the Hartree-Fock energy. Here and in what follows we omit the spin indices for brevity; hence our expressions are valid for zero field. Using the second-order free-energy functional  $\Phi_N^{(2)}$  in Fig. 2, one easily finds that the  $U^2$  selfenergy may be obtained by cutting the  $d$ -electron propagator line in the diagram as

$$\Sigma_N = \delta \Phi_N / \delta G_N. \quad (6)$$

Consequently, the imaginary part of the second-order contribution (in  $U$ ) to the impurity self-energy is given by

$$\Sigma_N''(\omega) = U^2 \int \frac{d\omega_1}{\pi} \int \frac{d\omega_2}{\pi} \int d\omega_3 \delta(\omega - \omega_1 - \omega_2 - \omega_3) F(\omega_1, \omega_2, \omega_3) G_{HF}''(\omega_1) G_{HF}''(\omega_2) G_{HF}''(\omega_3). \quad (7)$$

Here  $F(\omega_1, \omega_2, \omega_3)$  abbreviates the following collection of thermal occupancy factors

$$F(\omega_1, \omega_2, \omega_3) = [1 - f(\omega_1)][1 - f(\omega_2)][1 - f(\omega_3)] + f(\omega_1)f(\omega_2)f(\omega_3), \quad (8)$$

with  $f(\omega) = (e^{\omega/T} + 1)^{-1}$  denoting the Fermi distribution function.

Note that the  $U$ -perturbation theory can be derived from a free-energy functional,  $\Phi$ . Therefore, this is a "conserving approximation" [8] for the many-body system, with positive definite spectral functions and with sum rules fulfilled by construction. The linear term in  $U$ , see Fig. 2, is the HF term, describing the motion of a  $d$ -electron with spin  $\sigma$  in the mean field produced by the  $d$ -electron with spin  $-\sigma$ . This mean field, or the expectation value  $\langle n \rangle$ , must be computed selfconsistently. The quadratic term in  $U$  describes the interaction, at the impurity site, of the localized spin fluctuations (LSF) represented by the particle-hole spin-susceptibility bubbles ( $G_N \bar{G}_N$ ).

Yamada [6] first showed that the  $U^2$ -selfenergy  $\Sigma_N^{(2)}(\omega)$  yields a triple-peaked structure for the spectral density of the impurity atom. The sharp central peak for  $T = 0$  obtains the unitary limiting value at  $\omega = 0$ . This approach was later generalized to arbitrary finite temperatures [7] and it was shown that the central zero-frequency peak has a sensitive  $T$  dependence.

The Anderson model in a superconductor is given by

$$\mathcal{H}_{A,BCS} = \mathcal{H}_{BCS} + \mathcal{H}_{sd} + \mathcal{H}_d + \mathcal{H}_U, \quad (9)$$

where the BCS hamiltonian is

$$\mathcal{H}_{BSC} = \sum_{k,\sigma} \varepsilon_{k\sigma} n_{k\sigma} - \sum_k (\Delta c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger + \Delta^* c_{-k\downarrow} c_{k\uparrow}). \quad (10)$$

This model has been discussed in the HF [9, 10] and Schrieffer-Wolff [11] limits. In the HF approximation for a superconductor one truncates the Coulomb-interaction term as follows:

$$U n_\uparrow n_\downarrow \rightarrow U \langle n_\uparrow \rangle n_\downarrow + U \langle n_\downarrow \rangle n_\uparrow + U \langle d_\uparrow^\dagger d_\downarrow^\dagger \rangle d_\downarrow d_\uparrow + U \langle d_\downarrow d_\uparrow \rangle d_\uparrow^\dagger d_\downarrow^\dagger. \quad (11)$$

Here the anomalous average  $\langle d_\downarrow d_\uparrow \rangle$  induced at the impurity site presents another mean field, in addition to  $\langle n \rangle$ , which is to be computed selfconsistently. The HF approximation to the Anderson model in a superconductor [9] shares the same instability problem as the HF approximation in the normal metal [1]: a spontaneous unphysical breaking of symmetry at the impurity site. Our aim is to develop an approach which is free from this HF instability and which enables one to go beyond the HF picture. In particular, we are interested to investigate the qualitatively new physical features, especially in the  $d$ -electron density of

states, due to increasing electron correlations as  $U$  increases beyond  $\pi\Gamma$ , where the HF solution no longer provides quantitatively meaningful answers.

A generalization of the  $U$ -perturbation theory for the Anderson model in a superconductor has thus far not been discussed in the literature. The purpose of this Letter is to suggest a new, conserving, self-energy  $U$ -perturbation expansion that is valid in a superconductor. We note that the RNG approach has recently been generalized to treat magnetic impurities in superconductors, but thus far only for the  $s-d$  model [12].

The matrix selfenergy expansion in the Nambu space is introduced as

$$\hat{G}_S(\omega) = \left( (\hat{G}_{HF}(\omega))^{-1} - \hat{\Sigma}_S(\omega) \right)^{-1}, \quad (12)$$

where the hat denotes matrices in the particle-hole Nambu space and the  $d$ -electron propagator in the HF approximation is given as

$$\hat{G}_{HF}(\omega) = - \begin{pmatrix} \omega - E_{HF} - F_{11}(\omega) & U\langle d_\sigma d_{-\sigma} \rangle - F_{12}(\omega) \\ U\langle d_{-\sigma}^\dagger d_\sigma^\dagger \rangle - F_{21}(\omega) & \omega + E_{HF} - F_{22}(\omega) \end{pmatrix}^{-1}, \quad (13)$$

which, for brevity, we denote here as:

$$\hat{G}_{HF}(\omega) = \begin{pmatrix} \mathcal{G}(\omega) & \mathcal{F}(\omega) \\ \bar{\mathcal{F}}(\omega) & \bar{\mathcal{G}}(\omega) \end{pmatrix}. \quad (14)$$

These propagators are illustrated graphically in Fig. 3 as lines with two arrows.

The energy-integrated Green's function (or generalized density of states)  $\hat{F}_S(\omega)$  in Eq. (13) is

$$\hat{F}_S(\omega) = \begin{pmatrix} F_{11}(\omega) & F_{12}(\omega) \\ F_{21}(\omega) & F_{22}(\omega) \end{pmatrix} = \sum_k \hat{V}_k^* \hat{G}_k^0(\omega) \hat{V}_k, \quad (15)$$

where

$$\hat{V}_k = \begin{pmatrix} V_k & 0 \\ 0 & -V_k^* \end{pmatrix}. \quad (16)$$

Above, in Eq. (15),  $\hat{G}_k^0(\omega)$  is the unperturbed Green's function for the bulk superconductor:

$$\hat{G}_k^0(\omega) = \begin{pmatrix} \omega - \varepsilon_k & \Delta \\ \Delta^* & \omega + \varepsilon_{-k} \end{pmatrix}^{-1}. \quad (17)$$

The selfenergy in Eq. (12) is a matrix in the Nambu space

$$\hat{\Sigma}_S(\omega) = \begin{pmatrix} \Sigma_{11}(\omega) & \Sigma_{12}(\omega) \\ \Sigma_{21}(\omega) & \Sigma_{22}(\omega) \end{pmatrix}, \quad (18)$$

which may be obtained as

$$\Sigma_{ij} = \delta\Phi_S/\delta(G_S)_{ij}, \quad (19)$$

where  $\Phi_S$  now denotes the free energy in a superconductor.

The second-order free-energy term in  $U$  for a superconductor,  $\Phi_S^{(2)}$ , is illustrated in Fig. 4 from which we obtain the following expression, accurate to  $U^2$ :

$$\begin{aligned} \begin{pmatrix} \Sigma''_{11}(\omega) & \Sigma''_{12}(\omega) \\ \Sigma''_{21}(\omega) & \Sigma''_{22}(\omega) \end{pmatrix} &= U^2 \int \frac{d\omega_1}{\pi} \int \frac{d\omega_2}{\pi} \int d\omega_3 \delta(\omega - \omega_1 - \omega_2 - \omega_3) F(\omega_1, \omega_2, \omega_3) \\ &\times \begin{pmatrix} \mathcal{G}''(\omega_1) & -\mathcal{F}''(\omega_1) \\ -\bar{\mathcal{F}}''(\omega_1) & \bar{\mathcal{G}}''(\omega_1) \end{pmatrix} \left( \mathcal{G}''(\omega_2) \bar{\mathcal{G}}''(\omega_3) - \mathcal{F}''(\omega_2) \bar{\mathcal{F}}''(\omega_3) \right), \end{aligned} \quad (20)$$

where  $F(\omega_1, \omega_2, \omega_3)$  is, again, given by Eq. (8). Note that the propagators  $\mathcal{G}$ ,  $\bar{\mathcal{G}}$ ,  $\mathcal{F}$ , and  $\bar{\mathcal{F}}$  in the above expression may be evaluated in the HF approximation, see Eq. (13), which already contains the pairing interaction  $\mathcal{H}_{BCS}$  to infinite order in the unperturbed hamiltonian  $\mathcal{H}^0$ . Therefore, the  $\omega$  integrals in Eq. (20) are rather complicated: they contain delta-function contributions from the bound states and also continuum contributions. Trivially, one observes that the normal-state limit, Eq. (7), is obtained consistently from Eq. (20) when  $\Delta \rightarrow 0$  and that the diagrams in Fig. 4 reduce to those in Fig. 2 for  $\Delta \rightarrow 0$ .

The free-energy diagrams in Fig. 4 now comprise of two contributions linear in  $U$ , corresponding to the selfconsistent occupation-number field  $\langle n \rangle$ , and the induced anomalous average (the proximity pairing at the impurity  $d$ -orbital site)  $\langle d_\downarrow d_\uparrow \rangle$ . Furthermore, there now occur three terms quadratic in  $U$ . Two of these terms are due to the localized spin fluctuations (LSF), represented by the spin-susceptibility bubble  $(\mathcal{G}\bar{\mathcal{G}})$ , mutually interacting at the impurity site and also with the induced localized pairing fluctuations (LPF), shown as the pairing-susceptibility bubble  $(\mathcal{F}\bar{\mathcal{F}})$ . The third contribution arises from the induced mutually interacting localized pairing fluctuations.

Preliminary numerical results [13] indicate the doubling of bound states, in comparison to the HF theory. In particular, the new bound states tend towards  $\omega = 0$  for increasing  $U$ . We shall discuss the full numerical results in detail elsewhere. Our approach can also be readily

extended to other situations of interest, such as an Anderson impurity in unconventional superconductors [14]. In this case, the self-energy expressions are formally the same but the order parameter must in general be interpreted as a matrix in spin space. Also the order parameter  $\Delta(\hat{k})$  for unconventional superconductors possesses less rotational symmetry than that in the  $s$ -wave case. This will naturally lead to a  $\hat{k}$ -dependence of the  $d$ -electron Green's function  $\hat{G}_S(\hat{k}, \omega)$ , the matrix selfenergy  $\hat{\Sigma}_S(\hat{k}, \omega)$  and the bound-state spectrum below the  $\hat{k}$ -dependent energy-gap edge.



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## FIGURES

FIG. 1. The local  $d$ -electron propagator in the normal state,  $G_N(\omega)$ , is here denoted as a line with an arrowhead (l.h.s.). The local Coulomb-repulsion or Anderson-Hubbard interaction term  $Un_{\uparrow}n_{\downarrow}$  is represented in the diagrams with a dashed line having two vertices (r.h.s.).

FIG. 2. The terms  $\Phi_N^{(2)}$  in the normal state up to the second order in  $U$ . The linear term in  $U$  is the Hartree-Fock bubble. The second-order term in  $U$  contains two particle-hole (susceptibility) bubbles, describing interacting localized spin fluctuations (LSF) at the impurity site.

FIG. 3. Elements of the localized  $2 \times 2$  Green's-function matrix in the Nambu space for the superconducting state are represented by lines with double arrows. Here  $\mathcal{G}(\omega)$ , corresponding to the  $G_N(\omega)$  in Fig. 1, is the electron propagator, while  $\bar{\mathcal{G}}(\omega)$  is the time-reversed hole-propagator function;  $\mathcal{F}(\omega)$  is the anomalous particle-hole Green's function and  $\bar{\mathcal{F}}(\omega)$  denotes its conjugate.

FIG. 4. Generalization of  $\Phi$  to the second order in  $U$  for the pair-correlated state,  $\Phi_S^{(2)}$ , expressed in terms of the superconducting propagators,  $\mathcal{G}$ ,  $\bar{\mathcal{G}}$ ,  $\mathcal{F}$ , and  $\bar{\mathcal{F}}$ , in Fig. 3. Due to the anomalous propagators in the pair-correlated medium, there now occur two first-order Hartree-Fock terms linear in  $U$  and three second-order terms in  $U$ , owing to the interacting localized spin fluctuations (LSF), correlated localized spin and pairing fluctuations (LSPF), and interacting localized pairing fluctuations (LPF), respectively.

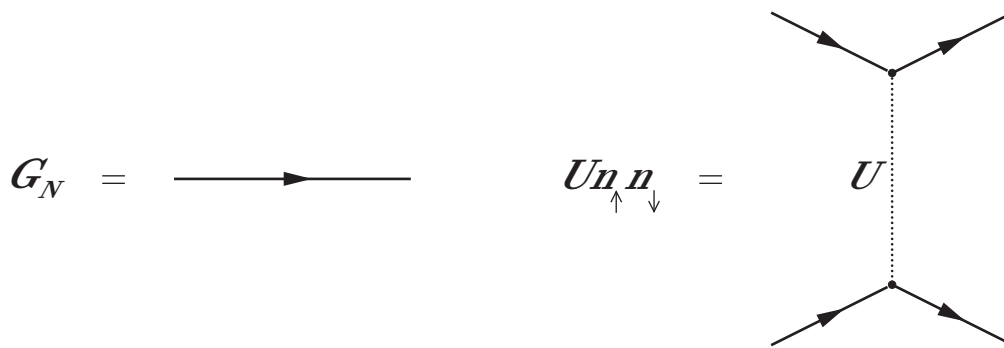


Figure 1:

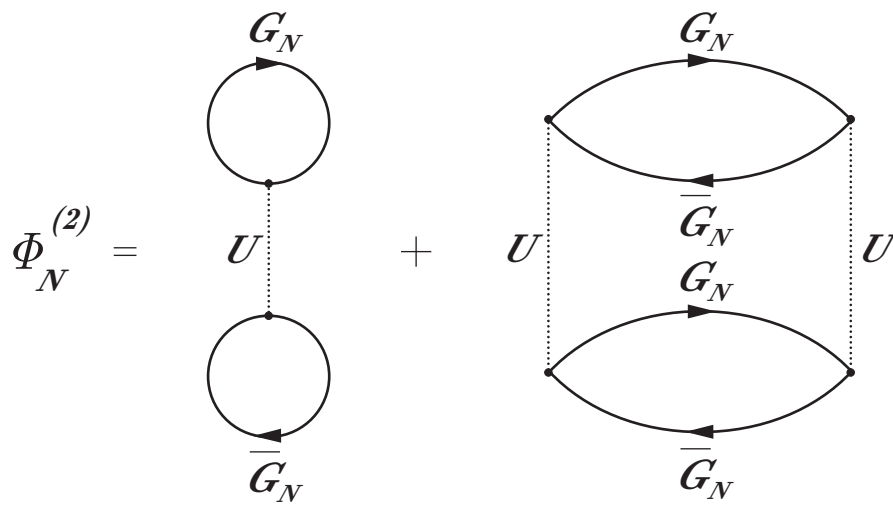


Figure 2:

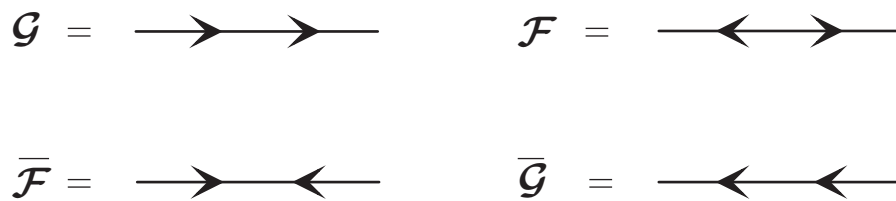


Figure 3:

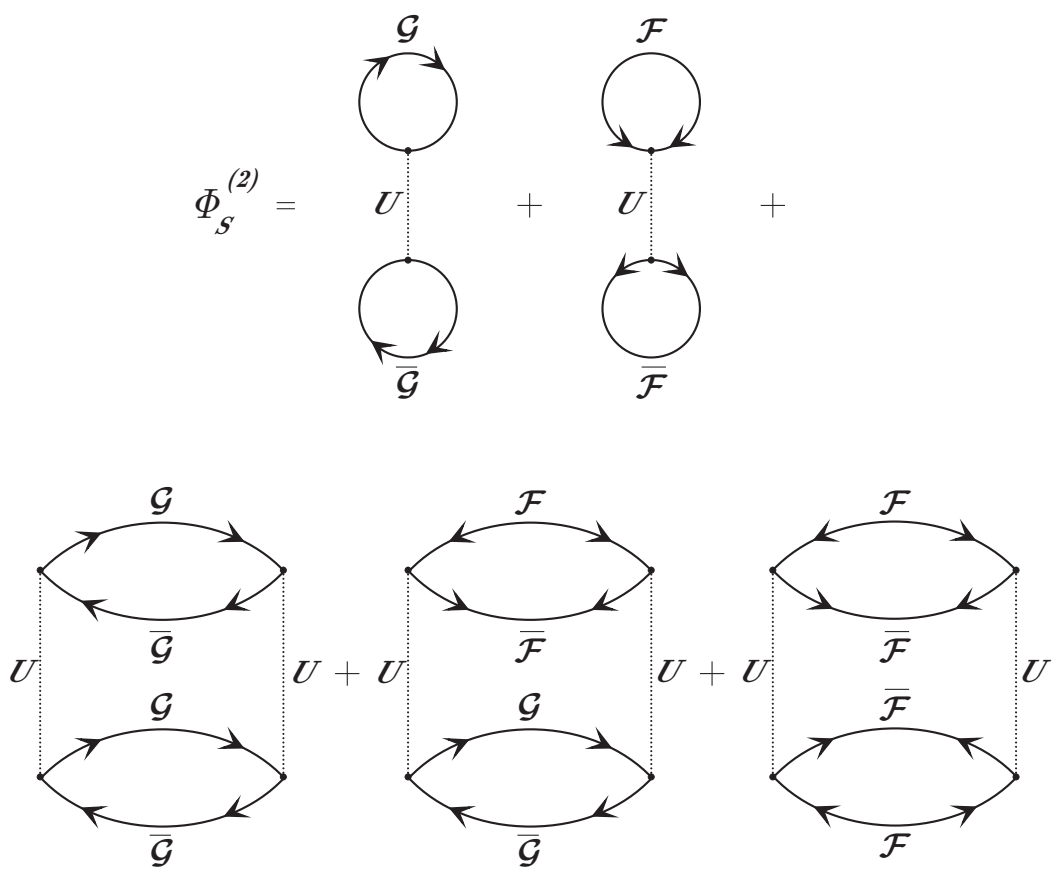


Figure 4: